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ORIGINAL PAPER

Electrochemical and FTIR spectroscopic studies of tyrosine oxidation at polycrystalline platinum surfaces in alkaline solutions

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Abstract The electrochemical oxidation of tyrosine has been studied on polycrystalline platinum in sodium hydroxide using cyclic voltammetry and in situ Fourier transform infrared spectroscopy (FTIRS). According to infrared data, the first interaction of tyrosine through the carboxylate group on platinum is proposed. The results showed an onset for tyrosine oxidation at ca. 0.5 V with the formation of soluble formate ion as product. The sharp increase in the current vs potential slope from ca. 1.1 V obeys the detection of cyanate ions together with *p*-(methyl)-phenoxide ions. No adsorbed carbon monoxide as well as carbon dioxide was detected by this methodology in the whole studied potential range. These results contrast with those obtained in acid solution where two parallel reactions, one yielding the γ-lactone of hydroxy benzofurane and the other producing *p*-benzoquinone occurs for the oxidation of tyrosine on platinum.

Keywords Tyrosine · FTIR spectroscopy · Platinum single crystals · Alkaline media

Dedicated to Prof. Dr. Teresa Iwasita on the occasion of her 65th birthday in recognition of her numerous contributions to interfacial electrochemistry.

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Introduction

Tyrosine (*tyr*) is a well-known essential amino acid with a crucial role in the functionality of lung cancer therapy, the activity of neuro-transmissors of nervous system, and the synthesis of dopamine and serotonine [1–3]. Adsorption of proteins at surfaces is the first step in some biochemical and biophysical processes; therefore, *tyr* adsorption on membranes can be mimicked by studying its interactions on noble metals using in situ electrochemical [4–6] and vibrational techniques [7, 8]. In particular, the combination of cyclic voltammetry, current transients, and in situ Fourier transform infrared spectroscopy (FTIRS) have demonstrated to be powerful tools to study the adsorption, nature, and configuration of amino acids [6–12]. More properly, in the case of aromatic ring-containing amino acids, such as *tyr*, tryptophan, histidine, and phenylalanine, the information about the nature and configuration of the adsorbates mostly covers the case of polycrystalline (pc) and single-crystal platinum or gold surfaces [9–13]. The use of the sum frequency generation methodology to study phenylalanine adsorption on platinum [8] provided molecular level information of the adsorbate formation on the electrode surface. The structure of adsorbed phenylalanine consists of a twofold coordination via a carboxyl group on the metal surface with a methylene group tilting away from the electrode, which allows the phenyl ring lying parallel to the surface.

On the other hand, the adsorption study of phenylalanine on Au(111) [13] demonstrates two types of adsorbates in neutral solutions. At negative values with respect to the potential of zero charge, phenylalanine is placed parallel to the surface, whereas at positive values, it is oriented with the carboxyl group approaching normally to the surface and the ammonium group extending towards the solution.

We have recently performed a detailed analysis using conventional electrochemistry and in situ infrared spectroscopy concerning the study of the adsorption configurations and oxidation pathways of *tyr* in acid media on Pt(111) and Pt(pc) surfaces [14]. No surface sensitivity of *tyr* bulk oxidation was detectable on both electrodes, although the adsorption process was structure sensitive. In situ FTIR technique shows two complex parallel reactions at potentials higher than 1.10 V vs reversible hydrogen electrode (RHE): one of them leading to a γ-lactone of the hydroxy-substituted benzofurane and the other yielding *p*-benzoquinone, both yielding also carbon dioxide.

The study of *tyr* electrooxidation has also been conducted using conventional electrochemical techniques at Pt(pc) in neutral buffered solutions [15]. In this case, a first adsorption of the carboxyl group to platinum followed by a decarboxylation leading to the next lower-chain aldehyde was proposed with a second fast electron transfer.

The oxidation of *tyr* at Pt(pc) in alkaline solutions has been previously studied by Ogura et al. [16], applying in situ FTIRS. It has been found the adsorption of the fully unprotonated carboxylate at potentials larger than 0.4 V vs Ag/AgCl. The oxidation of *tyr* at potentials larger than 1.10 V produced bulk phenoxyde, formate ions, and carbon dioxide. However, some of the infrared features in that report were wrongly assigned to adsorbed species, as the experiments were conducted only with p-polarized light. In this paper, we discuss the problem of adsorption configuration and oxidation of *tyr* on Pt(pc) in basic media using infrared spectra with both s- and p-polarized lights.

Experimental

The platinum working electrode for cyclic voltammetry was a pc sheet (0.5 cm^2), whereas for the spectroelectrochemical studies, a Pt(pc) disk (10-mm diameter) from Matek were used. Clean surfaces were obtained by flame annealing in a gas-oxygen flame and cooling in an argon atmosphere. The counter electrode was a large-area platinum sheet. All electrode potentials were measured against a RHE and referred to this scale in the text. The scan rate for the cyclic voltammetric runs was 0.05 Vs^{-1}, and in all cases, the experiments were performed at room temperature.

The electrolyte was prepared from sodium hydroxide (Merck p.a.) and ultrapure water (Millipore MilliQ) for the transmission spectra. *Tyr* solutions (10 mM) were prepared by adding the amino acid (Sigma Chemical) to the supporting electrolyte (0.1 M NaOH) in ultrapure water. Solutions were deareated with argon (99.998%), and all the experiments were performed in an air-free atmosphere.

FTIR experiments were carried out with a Bruker Vector 22 spectrometer equipped with a mercury–cadmium–telluride (MCT) detector. The electrochemical IR cell, fitted with a 60° CaF$_2$ prismatic window, was provided with an inlet and outlet for solutions to allow electrolyte exchange under potential control. For each spectrum, 128 interpherograms were collected at 8 cm^{-1} of resolution. Parallel (p) and perpendicular (s) polarized IR light was obtained from a BaF$_2$-supported Al grid polarizer. Spectra are represented as the ratio R/R_o, where R and R_o are the reflectance corresponding to the sample and reference spectra, respectively.

The experimental procedure to study the electrochemical oxidation and vibrational response of *tyr* consists of the following steps: (1) After the cyclic voltammetry for the platinum electrode in the base electrolyte was recorded, the potential was set to 0.05 V (E_{ref}); (2) then, the supporting electrolyte was replaced by the *tyr*-containing solution; (3) afterwards, the electrode was pushed against the CaF$_2$ window and the reference spectrum acquired; (4) then, the potential was increased from E_{ref} to 1.50 V in 50 mV steps where the sample spectra were recorded; (5) finally, the potential is decreased from 1.50 V to E_{ref} in the same potential steps.

Results and discussion

Figure 1 depicts the stationary cyclic voltammetry for Pt (pc) obtained in a 10-mM *tyr*+0.1 M NaOH solution run at 0.05 Vs^{-1}. The hydrogen ad-atom region at potentials lower

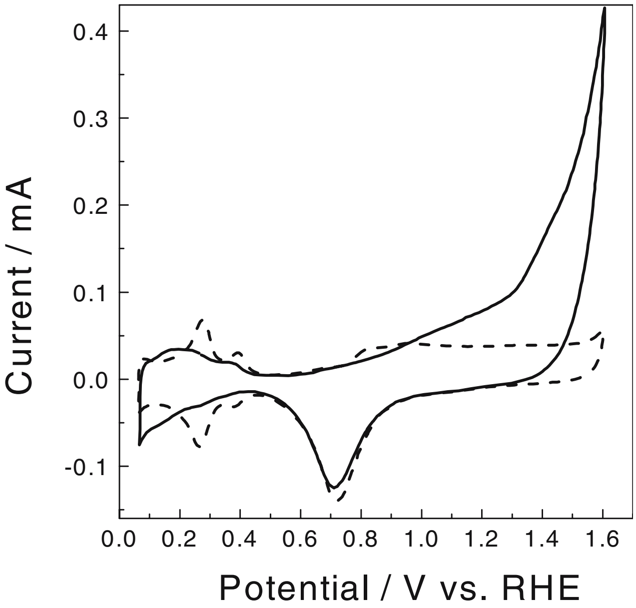


Fig. 1 Cyclic voltammetric profile of 10 mM *tyr*+0.1 M NaOH run at 0.05 Vs^{-1} for a Pt(pc) electrode. *Dashed lines* correspond to the electrochemical response of platinum in 0.1 M NaOH

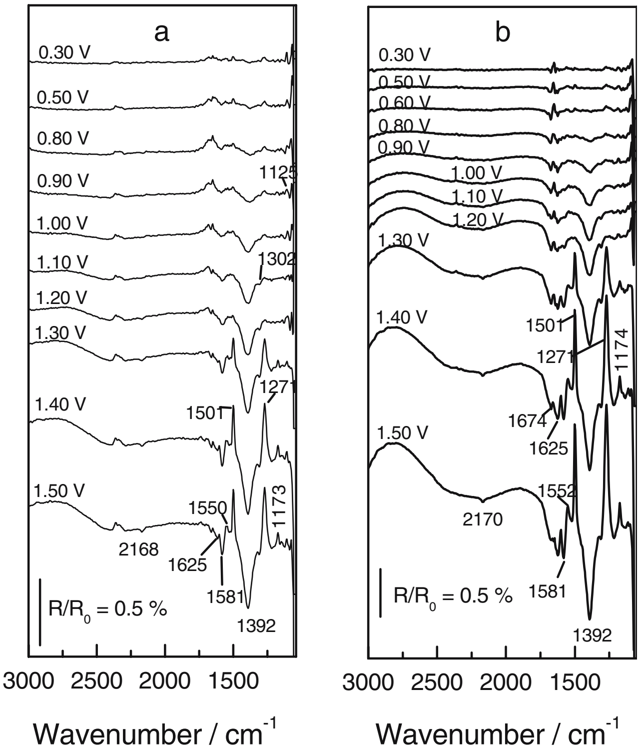


Fig. 2 In situ FTIR spectra in the 1,200- to 1,800-cm^{-1} range of 10 mM *tyr*+0.1 M NaOH for a Pt(pc) electrode. **a** p-Polarized light and **b** s-polarized light. The applied potentials and the characteristic bands are denoted in the *inset* plot. The spectra reference potential was 0.05 V

than 0.48 V is partially blocked by the presence of the amino acid in the solution (at pH≅13, the main species in the solution is $HOC_6H_4–CH_2–CH(NH_2)–COO^-$≡*tyr*$^-$) [17]. The interaction of this species with platinum also produces a negative potential shift of the weakly bound hydrogen from 0.26 to 0.17 V in the anodic potential incursion. However, little influence besides a partial suppression of the current intensity can be observed for the strongly bound hydrogen ad-atom. On the other hand, the onset of the oxidation during the positive-going potential scan seems to occur at ca. 0.5 V, with a breaking up current contribution at potentials ca. 1.1 V. As a difference with acid media, no maximum in the anodic current is developed on Pt(pc); only a change in the slope of the current vs potential contour is observed without any peak definition. A similar experiment was run for *tyr*$^-$ on Pt(111) between 0.05 and 1.15 V at 0.05 V s^{-1}, showing similar features for *tyr*$^-$ oxidation, denoting the absence of surface sensitivity for this solution reaction. Because the trail of *tyr*$^-$ oxidation behavior on platinum is quite limited by cyclic voltammetry, we have also studied the adsorption of *tyr*$^-$ (from a 2-mM aqueous concentration) by anodic stripping experiments online with FTIRS. We have used a micro-flux cell with the methodology of exchanging the supporting electrolyte after 10 min of adsorption at pre-fixed potentials. The results showed that the amino acid can be adsorbed in the 0.10 to 0.70 V range, exhibiting a maximum coverage at 0.50 V; however, the profiles are similar at all adsorption potentials. We did not see any different infrared signals of appreciable magnitude comparing to bulk *tyr*, using either s- or p-polarized lights.

A series of FTIR spectra acquired at Pt(pc) in a 10-mM *tyr*$^-$+0.1 M NaOH solution are plotted in Fig. 2 for the s- and p-polarized light between 3,000 and 1,100 cm^{-1}. The onset for *tyr*$^-$ oxidation is established at 0.5 V, where a tiny band at ca. 1,400 cm^{-1} using p-polarized light can be observed. Similar features using s-polarized light are not observed until 0.8 V, showing that, after a first adsorption process, adsorbed *tyr* oxidation products left the electrode as soluble species at potentials larger than 0.8 V. The FTIR spectra in the region from 2,500 to 2,000 cm^{-1} shows no contribution of carbon dioxide formation (near 2,340 cm^{-1}), but a band at 2,168 cm^{-1} [18]. This band has been found for the oxidation of glycine in acid solution [19] and also in

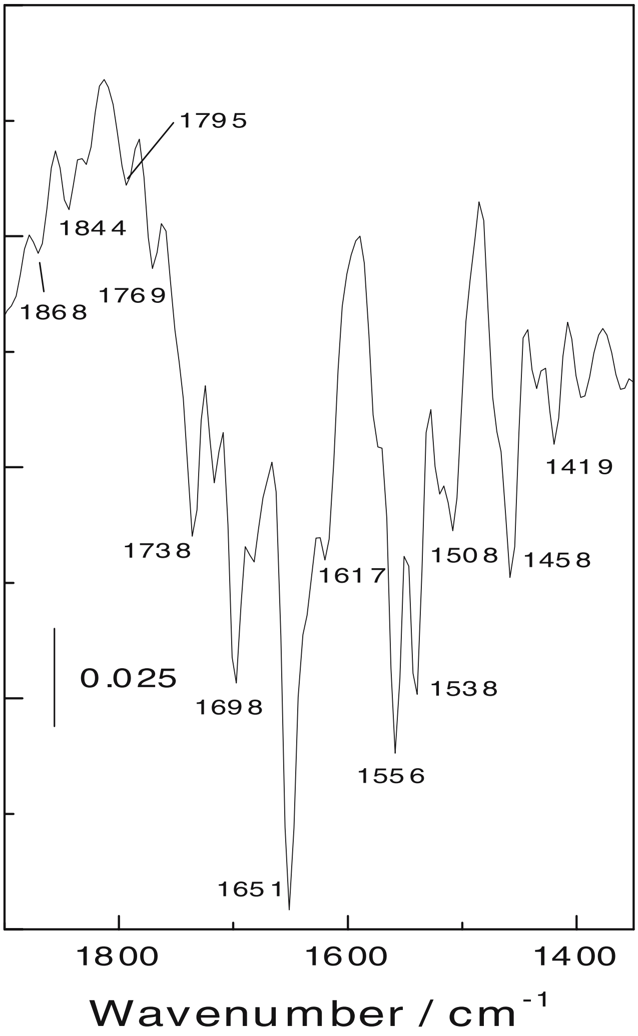
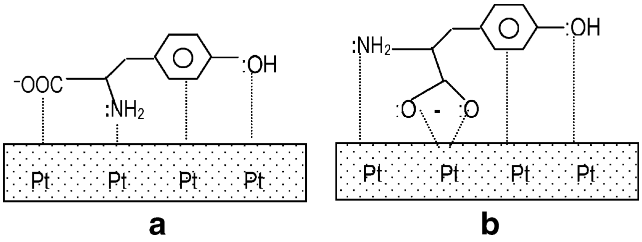


Fig. 3 Transmittance spectra for 10 mM *tyr*+0.1 M NaOH aqueous solution. The spectra were taken considering the base electrolyte as reference



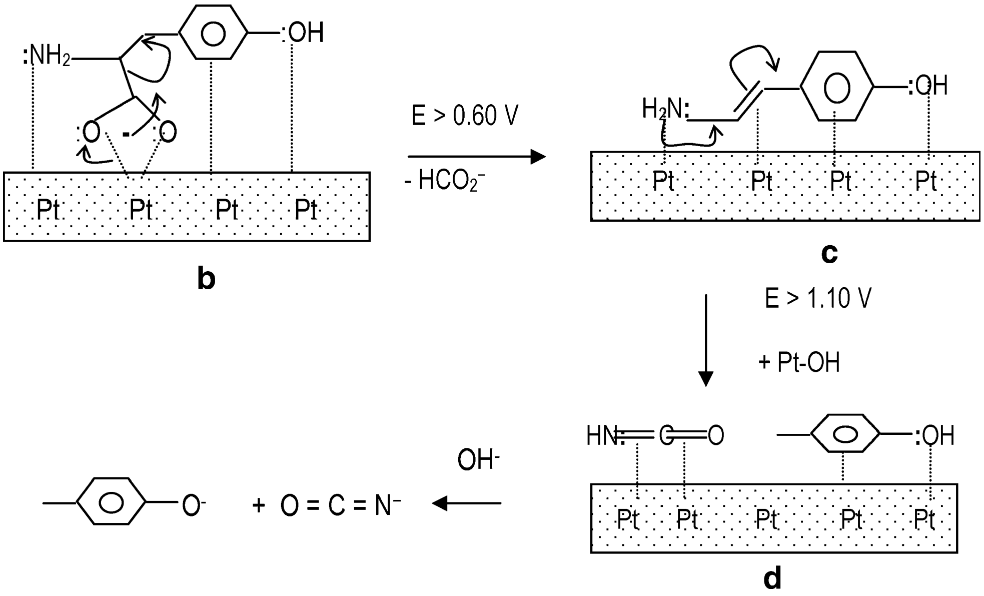
Scheme 1 The first possible interactions of tyrosine molecule with platinum in alkaline solutions

alkaline solution [12]. This peak is attributed to the C–N stretching vibration of the cyanide group such as cyanate species. Besides, they concluded [12] that glycine oxidation on platinum was inhibited in acid media by the strong adsorption of cyanide species. This inhibition of *tyr*$^-$ oxidation was not found in alkaline media by other authors [16] because of a visible carbon dioxide production (signal at 2,343 cm^{-1}), whose band intensity increases with the potential. Because we were able to see (Fig. 2) the 2,168-cm^{-1} band signal with p- and s-polarized light, we agree that, in alkaline media, the species is formed as a soluble moiety from the electrooxidation. On the contrary, in alkaline media, we did not see any contribution of carbon dioxide from the electrochemical oxidation of *tyr*$^-$ on both surfaces, but a strong signal at ca. 1,400 cm^{-1}, which is probably related to a carboxylate-type species from *tyr*$^-$ oxidation products. However, it has to be said that this species has been detected for histidine oxidation at Pt(pc) [16] with a blocking behavior of the active sites.

The interaction of *tyr*$^-$ with platinum can be also envisaged considering the electron lone pair of the amino group, i.e., the production of derivates from the cleavage/oxidation of the amino group to nitric oxides [20, 21]. They proposed the formation of HNO_{ads} as a previous intermediate species, which in a second chemical step, produces NO_{ads}. If this accounts for *tyr*$^-$ oxidation on platinum, the bending of the –NOH species has to be observed at 1,460 cm^{-1} due to the –NOH bending mode, which is far from the found spectral feature.

We can characterize our in situ FTIRS data at potentials larger than 1.10 V (where a sharp increase in the voltammetric current is observed) with negative bands at 1,392, 1,581, 1,625, and 1,674 cm^{-1} in the 1,800 to 1,000 cm^{-1} spectral range. These features are present in the spectra obtained with s- and p-polarized light and, therefore, have to be related to solution species (Fig. 2). The downward peak at 1,392 cm^{-1} is observed from ca. 0.5 V, coincidentally with the increase in the oxidation current of *tyr*$^-$ in the voltammetric contour of Pt(pc). The production of a soluble species containing a free carboxylate such as formate [10, 22] has been proposed, but in this case, no potential shift of the peak wave number has been found; that is, the strength of the bond does not change when applying more positive potentials. According to the literature [23, 24], this signal can be assigned to the symmetric carboxylate stretching of the formate group. The same absence of potential shift in the band at 1,581 cm^{-1} was found. This band can be assigned to the asymmetric stretching vibration of the carboxyl group of formate [23, 25]. This formate compound is the obtained *tyr*$^-$ oxidation product after the initial decarboxylation process when no carbon dioxide gets into the electrochemical cell from the outside.

On the other hand, the negative bands at 1,625 and 1,674 cm^{-1}, mostly found when using s-polarized light, can



Scheme 2 The formation of the final soluble products during the interaction of tyrosine molecule with platinum in alkaline solutions

be associated to the –NH_2 stretching deformation vibrations [15, 21] of *tyr*. It is worth noting that no potential shifts in these signals were observed, so it is likely that this species would be in solution. The oxidation of adsorbed nitrogen-containing compounds is strongly influenced by the adsorption of its products, mostly nitric oxide [21]. It forms an adsorbed NO_{ads} layer, stable between 0.55 and 0.75 V but oxidized to HNO_{2ads} at higher potentials. Above 0.9 V, the formation of NO_2 is postulated and the formation of N_2O between 0.5 and 1 V (from the homogeneous reaction between HNO_2 and hydroxylamine). If we were able to see these species, in situ FTIRS would give their characteristic features; bulk N_2O exhibits an asymmetric stretching band at 2,231 cm^{-1} [23]. We have found a signal at ca. 2,165 cm^{-1}, which was assigned to soluble cyanate species. In principle, the detection of NO, both in adsorbed and dissolved forms, are also possible. The NO_{ads} band frequencies are situated in a wide frequency range between 1,450 and 1,800 cm^{-1}, depending on both coverage and applied potential [23]. We have found a clear band at 1,581 cm^{-1} whose assignation has to be explained together with those at 1,392, 1,625, and 1,674 cm^{-1}, as they appeared simultaneously as explained above.

The production of multi-fold coordinated NO adsorbate in the 1,550–1,650 cm^{-1} frequency range [23] can be also obtained. These features, as well as a bipolar band at 1,760 cm^{-1} or a negative-going band at 1,720 cm^{-1}, were observed by Gootzen et al. [26] for NO ad-layers on polycrystalline platinum. Considering our reference potential value, we have not found any bipolar or negative-going signal in that spectral range.

FTIR spectra of *tyr*$^-$ on Pt(pc) also depict positive bands at 1,173, 1,271, 1,501, and 1,550 cm^{-1}. According to the literature [23, 24] and our transmission spectra of *tyr*$^-$ in NaOH (Fig. 3), the band at 1,501 cm^{-1} can be assigned to the ϕC=C skeletal stretching deformation of the benzene group in the amino acid, located at 1,512 cm^{-1} in Fig. 3. The peak at 1,271 cm^{-1} is assigned to the ϕC–O stretching vibration of C–O from phenol group in *tyr*$^-$ and the peak at 1,173 cm^{-1} to the in plane ϕC–H bending deformations of the aromatic ring, not seen in the transmission spectrum. Taking into account the spectra reference data [23–25] of aromatic compounds, the characteristic signals, such as 1,595 and 1,474 cm^{-1}, were found only in the transmission spectra (located at 1,617 and 1,460 cm^{-1} in Fig. 3) but not in the in situ FTIR spectra. However, the signal at 1,501 cm^{-1} (attributed to *tyr*$^-$ consumption) was found for FTIRS data using either s- or p-polarized light. Then, it is likely that the phenolic or (substituted phenolic) ring would be in solution and produced by the dissociation of the molecule after oxidation.

Finally, two possible adsorbed species can be initially formed depending on the strength of carboxylate ion and amine interactions in basic media. Scheme 1 shows these interactions to the platinum surface.

Two facts have to be considered in this study: The bands associated to formate species are seen at potentials more positive than 0.5 V with p-polarized light and the characteristic absorption bands of the aromatic group of *tyr*$^-$ are detectable at potentials larger than 1.10 V. Thus, it is clear that the orientation of *tyr*$^-$ is defined by the first attachment of the carboxylate with the phenolic group tilting away from the surface, species (B), which, at more positive potentials, reorients and desorbs to the solution. The initial flat orientation of *tyr*$^-$ becomes totally parallel to the surface at sufficiently positive potentials to promote the rupture of the *tyr*$^-$ molecule in soluble formate and p-methyl-phenolic species. Therefore, the formation of soluble products is proposed in Scheme 2.

Conclusions

The electrooxidation of tyrosine in alkaline media was studied on polycrystalline (and Pt(111)) platinum, showing independence toward surface orientation for the bulk reaction. The interaction of tyrosine probably involves the attachment of the carboxyl group to the surface with the phenolic ring far away at potentials larger than 0.5 V. The formation of formate soluble species is proposed and discussed. The net oxidation current occurs at potentials larger than 1.1 V, involving the formation of soluble cyanate species and (*p*-methyl)-phenoxide ions together with formate. These results were demonstrated by in situ s and p-polarized FTIR spectra on Pt(pc) surfaces in 0.1 M sodium hydroxide.

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